

# NATIONAL BUREAU OF STANDARDS REPORT

9018

STATUS REPORT FOR THE PERIOD ENDING 11/30/65

ON

THE MECHANISM OF STRESS CORROSION OF TITANIUM ALLOYS  
EXPOSED TO CHLORIDES AT ELEVATED TEMPERATURES

by

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Michael J. McBee  
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and  
B.T. Sanderson

for

Headquarters  
National Aeronautics and Space Administration  
Requisition No. PR10-2081  
May 4, 1964  
Contract No. R-130

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U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

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9018

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**U. S. DEPARTMENT OF COMMERCE**  
**NATIONAL BUREAU OF STANDARDS**

THE MECHANISM OF STRESS CORROSION OF TITANIUM ALLOYS  
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This investigation of the mechanism of the hot salt stress-corrosion cracking of Ti-8Al-1Mo-1V alloy was initiated during May 1964 by the Corrosion Section of the National Bureau of Standards in cooperation with the National Aeronautics and Space Administration. This report covers work performed since the last of four quarterly status reports\* which have been issued. The project was recently refunded following a period of inactivity subsequent to June 30, 1965.

Summarizing briefly the work of the previous report periods: The Ti-8Al-1Mo-1V alloy used in this investigation was chosen due to its likelihood as a supersonic transport structural material. Studies have been made using a hollow tensile specimen described in the first quarterly report which could be connected to a system for controlling the atmosphere in its interior or evacuating it to less than  $10^{-2}$  torr. Salts are deposited from 10% aqueous solution onto the interior of the specimen which is then heated to 750°F prior to the application of 73,500 lb/in<sup>2</sup> stress which is 90 percent of its yield strength at that temperature. A specimen with interior wall coated with 1 part MgCl<sub>2</sub>·6H<sub>2</sub>O to 7 parts NaCl and containing a dry oxygen atmosphere failed after an exposure period as short

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\* NBS Reports 8534, 8593, 8631 and 8690.

as 18 hours. This was a significantly shorter specimen life than those for the above system containing an added small excess of water which indicates that a critical amount of water vapor may be important. If HCl gas from the hydrolysis of hydrated salts is important in the attack on titanium alloy, this result may be in agreement with the fact that anhydrous HCl gas is more severe than moist. Specimens containing pure NaCl with moist oxygen are attacked more rapidly than those with dry oxygen. The pressure of oxygen gas ranging from 150  $\mu$  to 10 psi does not effect corresponding variations in specimen life. Mass spectrographic analyses of gaseous products from the interiors of several specimens showed no chlorine or hydrogen chloride as reaction products, however, the sensitivity of the test was not such as to preclude the existence of minute quantities of these products in the specimen. Further studies were initiated to determine the effect of oxide in the absence of gaseous oxygen, and to determine the role of water vapor or NaOH in the reaction.

Specimens of Ti-8-1-1 alloy sheet, stressed at 40 to 80 percent of their yield strength as four point loaded bent beams and coated with NaCl, were exposed in a circulating air furnace at 800°F. Exposure periods to failure generally increased with decreasing stress and ranged from 64 days for specimens stressed to 80 percent to 91 days for specimens stressed to 40 percent of their yield strength.

Corrosion products have been studied by x-ray diffraction and transmission electron-micrography. The usual oxides of titanium are found as well as lines\* for an unidentified phase "X" which may be formed by a reaction between NaCl and the oxide. X-ray diffraction patterns were also obtained during heating and cooling on the surfaces of stressed tensile specimens coated with  $\text{NaCl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Oxide structures and the decomposition of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  were studied at various temperatures.

During the present period, work has continued on hollow specimens containing an inert atmosphere. Argon is purified through titanium turnings at  $1200^\circ\text{F}$  to remove oxygen and nitrogen impurities and then cold trapped before introduction into the evacuated specimen cavity. The argon after several flushings is brought to about 5 psi before heating the specimen in order to activate a pressure switch which will open an elapsed time meter circuit when the internal pressure falls.

A number of specimens was preoxidized by exposing them to oxygen in a tube furnace at approximately  $800^\circ\text{F}$  for about 65 hours. Specimens are then exposed to the same conditions of temperature and stress as those described previously for specimens containing gaseous oxygen. An earlier specimen containing the  $\text{NaCl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  mixture failed after 360 hours. Two specimens containing NaCl failed in 170 and 253 hours. A third specimen which was baked at temperature under vacuum prior to introduction of the argon in an attempt to remove or

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\* NBS Report 8690 (5/12/65), Table 1.

combine oxygen occluded on the walls failed in 168 hours. A pre-oxidized specimen containing no salt did not show evidence of cracking after more than 600 hours of exposure to stress and temperature.

Likewise no evidence of cracking was found in two specimens which were not preoxidized containing NaCl or the mixed salt after 500 hours exposure. A third specimen containing the mixed salt evidenced small cracks on subsequent examination, but a slight air leak was suspected in the system in this case, and the argon was introduced at atmospheric pressure rather than at 5 psi as in the other specimens. Two specimens containing NaCl and purified argon which was moistened by bubbling through water failed in 326 and 290 hours.

Three specimens were run to study the effect of NaOH as a reactant in the stress corrosion process. The specimen interiors were coated from the 10% solution of 7 NaCl to 1  $\text{MgCl}_2$  with 10% NaOH added. One specimen in which the argon was placed at atmospheric pressure and in which an air leak was a possibility failed in 142 hours. Two other specimens with the introduced argon at 5 psi and leak tight showed no evidence of cracking when examined after 208 hours for one and 570 hours exposure for the other. All specimens which had not cracked in 500 hours of exposure to stress at temperature were elongated approximately 1.5 percent.

In order to verify and study with further certainty the behavior of preoxidized specimens in the absence of uncombined oxygen, an improved larger capacity vacuum system is being constructed. Also the specimen plug seal has been changed to an improved high vacuum and temperature couple design.

Tests are being conducted to compare the effects of different alkali and alkaline earth chlorides. Specimens of the sheet material stressed at 80 percent of their yield strength as four point loaded bent beams were coated by spraying and hot air gun drying of 10% solutions of the following salts: LiCl, KCl, CsCl;  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$ ,  $BaCl_2$ , and a eutectic mixture of LiCl-KCl (670°F). The eutectic mixture was poured in the molten state over another specimen, and a control specimen was included with no salt applied. Specimens with the higher vapor pressure eutectic mixture were placed in glass tubes having the ends plugged with glass wool before placing in the furnace at 800°F. Three specimens failed in less than 20 hours exposure - both specimens with the eutectic application and one with LiCl alone. The other specimens have not cracked in more than 70 days to date. The most catastrophic failure occurred with the specimen having the eutectic mixture applied in the molten state with evidence of heavy vapor redeposition on the tube interior. However, the fact that such short specimen lives were produced in all three cases where LiCl was present would lead to an analysis



stressing this point rather than one stressing the importance of salts in a molten or vapor state. Studies of the diffusion of Li in rutile\* have indicated the possibility that the Li ionic radius ( $0.62 \text{ \AA}$  compared to Na  $0.97 \text{ \AA}$ ) corresponds to that which would produce a minimum activation energy for diffusion in rutile. Also it is suggested that Li is similar to H in mechanism of interstitial diffusion. However, x-ray diffraction work in our laboratory indicates that LiCl on titanium produces an amorphous mass when heated to  $750^{\circ}\text{F}$  for several hours.

In addition to the catastrophic failure in the case of vaporized low melting eutectic, support can be gained for a vapor attack mechanism from metallographic studies which have been performed on sheet specimens in contact with NaCl which were placed in a furnace at  $800^{\circ}\text{F}$  in an oxygen atmosphere for 30 days. Fig. 1 illustrates the whisker structures observed on these specimens which were identified as primarily NaCl. Most whiskers were white in appearance, but others which were black had a thicker, tubular structure and gave lines for rutile. It is of interest that these structures are similar to the dark spike-like structures which were unidentified in a previous electron transmission micrograph\*\* of a surface film stripped from the interior of a failed hollow specimen.

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\* O.W. Johnson, Phys. Rev. 136, A284 (1964).

\*\* NBS Report 8631 (2/3/65), Fig. 4.

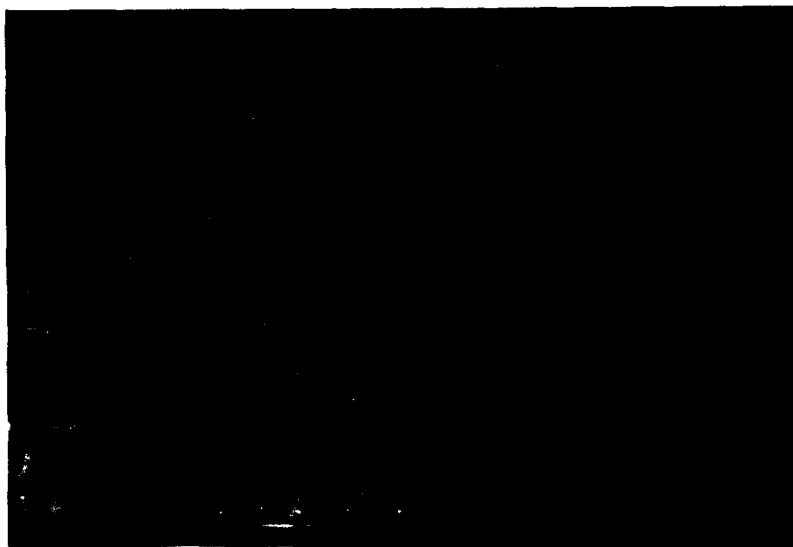


Figure 1. Surface of sheet specimen with NaCl corrodent after exposure in oxygen atmosphere at 800°F for 30 days. Whiskers are either primarily NaCl (white) or rutile (black). Print from 35 mm color slide. X 95.